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Thermal Relaxation of Liquid Borosilicate's Structure that Reflects the Slowness of the Boron Coordination Changes

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Abstract

Modeling of relaxation processes in the liquid borosilicate was performed. The kinetic scheme of temperature relaxation of the melts' structure is proposed. The scheme reflects the slowness of the boron coordination changes. The influence of various physicochemical factors on the relaxation processes' rate and the time of reaching equilibrium was analyzed.

Keywords: liquid borosilicate, relaxation of structure, depolymerization, boron coordination

In accordance with modern views [1] liquid borosilicate is polymerized electrolyte. This is due to the large number of connections with a considerable degree of covalency, as well as the simultaneous existence of the two types of atoms in the substance: multi-charged atoms with three or four bonds with the surrounding atoms (silicon, boron) and atoms with two connections (oxygen).

The main structural units of vitreous B_2O_3 are boroksolnye rings, which are connected by triangles. With the insert of the MeO, Me_2O in a melt part of the boron changes its coordination from a triple to quadruple and completes tetrahedron due to the oxygen inputted by the oxide-modifier. Ionized tetrahedron $[BO_4]^-$ is formed, in which the fourth oxygen is attached by donor-acceptor interaction. This is accompanied by an increase of the distance B-O, which indicates a change in the covalent bonds' nature. This means that connection between

tetrahedrals BO_4 is unequal. According to the authors [2], this causes the appearance of band, chain or ring formation's types in the borates' structure.

In these systems the processes of polymerization, disproportionation and change in the boron's coordination are running as the temperature decreases. The large size and complexity of the polymeric formations can cause slow relaxation of the melt's structure.

It was very important to create polymer model of oxide melts which would describe the relaxation processes at temperatures above the glass transition interval. The model, which takes into account the slowness of the boron coordination changes and its influence on the kinetics of the structural relaxation's processes is proposed in this paper.

The basis of this model was the assumption that the change in electrode potential of platinum in a nonequilibrium borosilicate melt is associated with the establishment of equilibrium between the boron-oxygen polyhedrons of the same composition but different structure:

$$B_nO_{m-n}^{[2(m-n)-3n]-} + nO^{2-} \Leftrightarrow B_nO_m^{(2m-3n)-}$$

or otherwise transition of boron coordination from a triple to quadruple:

$$B_{III} \rightarrow B_{IV} \tag{1}$$

The relation of measured electrode potential with a concentration (**c**) of free oxygen ions O^{2-} in non-equilibrium melt is showed in the equation:

$$\frac{c}{c_p} = e^{\frac{2F}{RT}\Delta\varphi}, \tag{2}$$

where $\Delta\varphi$ - the difference between the equilibrium and the current value of the potential of the investigated electrode ($\Delta\varphi = \varphi_p - \varphi$); c_p - the equilibrium concentration of free ions O^{2-}. The value of **c** drops with decreasing temperature. The reduction of the $\Delta\varphi$ over time to zero can be expected with structure's slow relaxation.

The reaction's (1) rate is determined by the concentration (**c**) of free ions O^{2-}. From formal kinetics' equations it follows that:

$$V = -\frac{dc}{dt} = k_1(c^n - {c_p}^n), \tag{3}$$

where k_1 - the rate constant of the direct reaction (1).

For a first-order reaction (n=1) we integrate and the result is following:

$$c = c_p + (c_0 - c_p)e^{-k_1 t} \quad . \tag{4}$$

Using equations (2) and (4) we find $\Delta\varphi$ dependence on time:

$$\Delta\varphi = \frac{RT}{2F} \ln\left[1 + (e^{\frac{2F}{RT}\Delta\varphi_0} - 1)e^{-k_1 t}\right] \quad . \tag{5}$$

Dependences, calculated on the base of obtained equation (5) are on Figures 1-3.

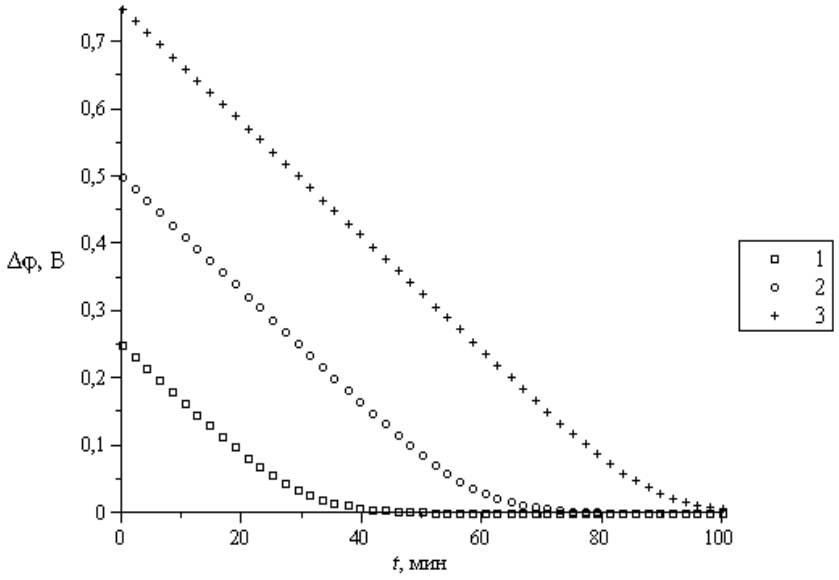

Figure 1. The calculated dependence of the potentials difference $\Delta\varphi$ vs the time t for liquid borosilicate at different initial potentials $\Delta\varphi_0 = 0{,}25$ V (1); 0,5 V (2); 0,75 V (3);

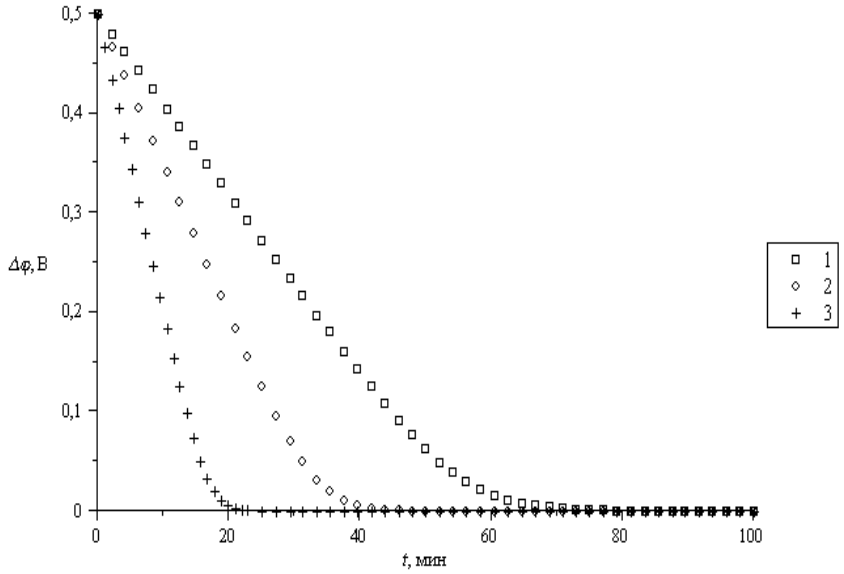

Figure 2. The calculated dependence of the potentials difference $\Delta\varphi$ vs the time t for liquid borosilicate at the different rate constant of the reaction k_1=0,003 (1); 0,005 (2); 0,01 (3).

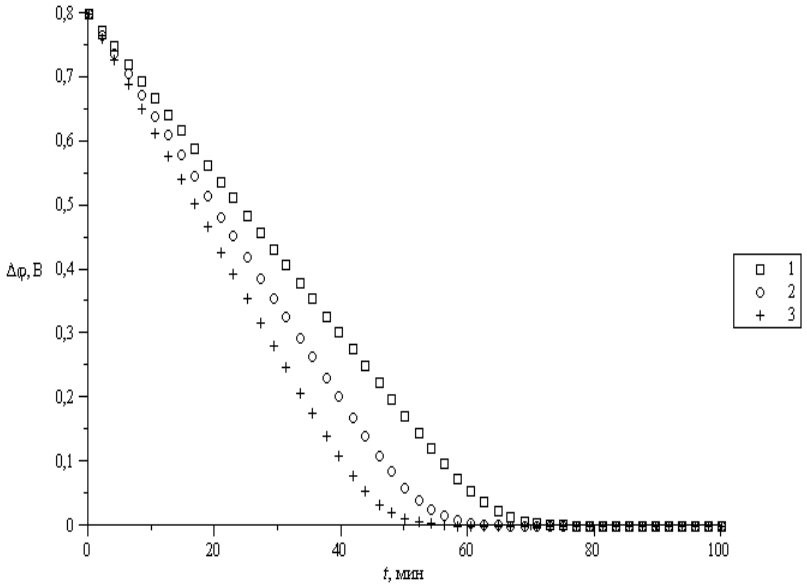

Figure 3. The calculated dependence of the potentials difference $\Delta\varphi$ vs the time t for liquid borosilicate at different temperatures T= 973 K (1); 1173 K (2); 1373 K (3)

Equation (5) is also true for the depolymerization reaction of silicon-oxygen complexes $O^{2-} + O^0 = 2O^-$ provided that it takes place in one stage, and has

the first order (n=1). It can be seen, that the main feature of the obtained dependences is their smooth, falling nature, in contrast to the S-shaped curves in the previous model [3]. Temperature rise, increase of the reaction rate constant and reduction of initial potential lead to decrease of the relaxation time. However, this time is quite long, up to several dozen minutes.

References

[1] M. M. Schultz, O. V. Mazurin. *Modern ideas about the glasses' structure and their properties*, Leningrad, 1988.

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